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PATENT APPLICATION

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicants: Tetsuo NISHIKAWA et al

For: THERMOPLASTIC RESIN COMPOSITION

Serial No.: 09/973 646 Group: 1714

Confirmation No.: 6210

Filed: October 9, 2001 Examiner: Shosho

Atty. Docket No.: Nanjo Case 1

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

**DECLARATION OF PRIOR INVENTION IN WTO MEMBER COUNTRY
TO OVERCOME CITED PATENT OR PUBLICATION (37 CFR § 1.131)**

This declaration is to establish completion of the invention of this application Serial No. 09/973 646, in a WTO member country, Japan, at a date prior to August 27, 1999, the earliest U.S. effective filing date of U.S. Patent No. 6 300 399 to Gallucci et al, and August 18, 2000, the U.S. filing date of U.S. Patent No. 6 364 422 to Sakaki et al that was cited by the Examiner.

The persons making this declaration are only some of the joint inventors and a suitable excuse is attached for failure of the omitted joint inventor to sign this declaration.

To establish the date of completion of the invention of this application, an exhibit is enclosed as evidence. The enclosed exhibit is a copy of JP 11-95712 and an English-language translation thereof. JP 11-95712 names Tetsuo NISHIKAWA, Kazuo HARUTA, Toshiaki SAKAKI and Tetsu MIZOGUCHI as inventors and has a filing date of April 2, 1999. JP 11-95712 discloses a thermoplastic resin composition comprising 2.5 to 15 wt.% of a styrene-based thermoplastic elastomer and 85 to 97.5 wt.% of tungsten powder.

From this exhibit, it can be seen that the invention of this application was made prior to August 27, 1999, the earliest U.S. effective filing date of U.S. Patent No. 6 300 399 to Gallucci et al, and August 18, 2000, the U.S. filing date of U.S. Patent No. 6 364 422 to Sakaki et al.

This declaration is submitted subsequent to a final rejection.

As a party signing below:

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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VERIFICATION OF TRANSLATION

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declare as follows:

That I am well acquainted with both the English and Japanese languages, and

That the attached document is true and correct translation made by me to the best of my knowledge and belief of:

Japanese Laid-Open Patent Publication No. 2000-290466
(Japanese Patent Application No. 11-95712)

Date: May 21, 2004

Reiko Komaki
(Signature of Translator)

Japanese Laid-Open Patent Publication No.P2000-290466A

Application No. 11-95712

Date of Application: April 2, 1999

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SUMITOMO RUBBER INDUSTRIES, LTD

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[Title of the Invention] Thermoplastic resin composition

[Claims]

1. A thermoplastic resin composition comprising 2.5 to 15 percentage by weight (wt%) of a thermoplastic elastomer and 85 to 97.5 wt% of tungsten powder.
2. The thermoplastic resin composition of claim 1, wherein the thermoplastic elastomer is a styrene-based thermoplastic elastomer.
3. The thermoplastic resin composition of claim 2, wherein the thermoplastic elastomer is a hydrogenated polystyrene-polyisoprene block copolymer, a hydrogenated polystyrene-polybutadiene block copolymer or a hydrogenated polystyrene-polyisoprene block copolymer containing a butadiene unit in its isoprene moiety.
4. The thermoplastic resin composition of claim 1, 2 or 3, wherein a surface hardness of the thermoplastic resin composition is 80 or less, when measured by a method defined in JIS K-7215.
5. The thermoplastic resin composition of claim 1, 2, 3 or 4, wherein a

specific gravity of the thermoplastic resin composition is 8 or more.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a thermoplastic resin composition having a high specific gravity and an excellent flexibility.

[0002]

[Prior Art and Problems to be Solved by the Invention]

Polymer materials are easy to process and excellent in corrosion resistance, compared with metallic materials. In addition, polymer materials are light and comparatively inexpensive, and have excellent insulation properties, so that they recently have been used widely in many fields as raw materials or structural materials for electrical and electronic parts, machine parts, precision parts, general industrial parts and the like.

[0003]

Moreover, polymer materials are excellent in processability, compared with metallic materials that require a cutting process, a sintering process or the like. In particular, when molded by injection molding, articles having a complex shape advantageously can be molded by only one process.

[0004]

Regarding a balance weight mounted on a wheel in order to adjust a wheel balance of an automobile or the like, it is preferable that the balance weight is as small as possible so as not to spoil the appearance of the wheel. It is also desirable that the balance weight is easy to shape so as to fit the rim diameter of the wheel. For these reasons, conventionally, lead, which is a metallic material having a high specific gravity and an excellent flexibility, has been used as a material for forming the balance weight.

[0005]

However, lead is toxic, and moreover, lead that has entered a human body from the skin and deposited in bones is very difficult to discharge and

accumulates in the body. If lead is accumulated in a human body, lead poisoning may occur. Therefore, it is preferable to use a material other than lead to form the balance weight for a wheel as described above. However, at present, there is no such material having a high specific gravity and an appropriate flexibility as lead.

[0006]

Therefore, it is an object of the present invention to provide a thermoplastic resin composition that is highly flexible and excellent in processability while having a specific gravity as high as lead and that can be used as a material for forming various kinds of articles requiring both massiveness and flexibility such as a balance weight as described above by using a thermoplastic resin, which is a polymer material.

[0007]

【Means for Solving the Problems and effect of the Invention】

To solve the above mentioned problems, the present invention provides a thermoplastic resin composition having a high specific gravity, flexibility and an excellent processability by blending 2.5 to 15 percentage by weight (wt%) of thermoplastic elastomer and 85 to 97.5 wt% of tungsten powder.

[0008]

The thermoplastic elastomer used in the present invention contains a rubber component having elasticity (soft segment) and a molecule-constraining component for preventing plastic deformation (hard segment) in its molecules. The thermoplastic elastomer is a polymer material that behaves like rubber at room temperature, because the molecular motion of the soft segment is locally constrained by the hard segment but that is plastically deformed by an increase in temperature. The thermoplastic elastomer is plasticized at a high temperature and becomes moldable, whereas at room temperature, the thermoplastic elastomer retains its shape and can be deformed easily.

[0009]

More specifically, examples of the thermoplastic elastomer include a

styrene-based thermoplastic elastomer containing polystyrene as the hard segment and (hydrogenated) polybutadiene or (hydrogenated) polyisoprene as the soft segment; an olefin-based thermoplastic elastomer containing polyethylene or polypropylene as the hard segment and ethylene-propylene-diene copolymer (EPDM) or isobutylene-isoprene rubber as the soft segment; a polyester-based thermoplastic elastomer containing polyester as the hard segment and polyether or aliphatic polyester as the soft segment; an urethane-based thermoplastic elastomer containing a urethane bonding as the hard segment and polyether or polyester as the soft segment; and a polyamide-based thermoplastic elastomer containing polyamide as the hard segment and polyether or polyester as the soft segment.

[0010]

It is also possible to use a 1,2-polybutadiene-based thermoplastic elastomer containing syndiotactic 1,2-polybutadiene as the hard segment and amorphous polybutadiene as the soft segment; a trans 1,4-polyisoprene-based thermoplastic elastomer containing trans 1,4-polyisoprene as the hard segment and amorphous polyisoprene as the soft segment; ionomer containing metal carboxylate ion cluster as the hard segment and amorphous polyethylene as the soft segment; a PE/EEA, EVA-based thermoplastic elastomer containing crystalline polyethylene as the hard segment and ethylene-ethylacrylate copolymer or ethylene-vinyl acetate copolymer as the soft segment; and a fluorine-based thermoplastic elastomer containing fluororesin as the hard segment and fluorine-based rubber as the soft segment.

[0011]

The thermoplastic elastomer used in the invention has to be excellent in weather resistance and aging resistance, in view of its use outdoors. For example, if the thermoplastic elastomer is used as a material for a balance weight mounted on a wheel of an automobile whose temperature rises to about 100°C, the thermoplastic elastomer is further required to be heat resistant so as not to be molten at about 100°C. In order to satisfy these requirements, it is desirable that the thermoplastic

elastomer does not have a double bond and is not hydrolyzed. More specifically, a hydrogenated styrene-based thermoplastic elastomer which is produced by hydrogenating the polyisoprene moiety or the polybutadiene moiety constituting the intermediate soft segment of the styrene-based thermoplastic elastomer (SEPS and SEBS respectively) is suitable. Alternatively, it is also possible to use a hydrogenated styrene-based thermoplastic elastomer containing a unit of butadiene in the intermediate isoprene moiety. It is possible to use two or more different kinds of hydrogenated styrene-based thermoplastic elastomers in combination, such as SEPS and SEBS.

【0012】

For example, in the case of the above-described SEPS, the physical properties may change, depending on the styrene content, the molecular weight of isoprene, the molecular weight distribution or the like. More specifically, the SEPS becomes hard as the styrene content is increased, and its strength is increased as the molecular weight of isoprene is increased. The moldability of the SEPS is reduced as its molecular weight distribution becomes sharp. In particular, when the molecular weight of isoprene is large and its molecular weight distribution is sharp, molding of the SEPS is extremely difficult. Regarding the styrene content, about 10 to 65% is generally used. However, for the SEPS used in the present invention, a suitable styrene content is 13 to 30%, preferably about 13 to 20%. Moreover, regarding the moldability of the SEPS, it is preferable that the MFR of the SEPS is 0.05 g/10 min. or more, more preferably 0.5 g/10 min or more, and even more preferably 1 g/10 min or more at 230°C and 2.16 kg. This is because by blending tungsten powder, the moldability is reduced, compared with using a thermoplastic elastomer alone.

【0013】

The styrene-based thermoplastic elastomer as described above is prepared by, for example, the following methods: preparing a block copolymer by living polymerization of styrene, isoprene and styrene or styrene, butadiene and styrene in this order using a monofunctional initiator

such as alkyl lithium (three-step polymerization with a monofunctional initiator) and then performing hydrogenation; or preparing a block copolymer by living polymerization with the same monofunctional initiator in the same manner and coupling with alkyl dihalide (two-step polymerization by coupling), and then performing hydrogenation. The thermoplastic elastomer used in the present invention can be in the form of pellets or powder.

[0014]

It is desirable that the tungsten used in the present invention is in the form of powder, because it is required to be blended uniformly with the thermoplastic elastomer. The particle diameter of the tungsten powder is preferably 300 μm or less, more preferably 2 to 100 μm , even more preferably 3 to 30 μm and most preferably 3 to 27 μm . This is because, if the average particle diameter of the tungsten powder is large, the thermoplastic resin composition is difficult to pass through a mold gate and therefore the moldability is reduced when being molded by injection molding. On the other hand, if the particle diameter of the tungsten powder is too small, the surface area of the tungsten powder is so large that a predetermined amount of thermoplastic elastomer cannot cover the surface of the tungsten powder completely. It is preferable to use tungsten powders of a small particle diameter and a large average particle diameter in combination, because the flowability of the thermoplastic resin composition is improved and the moldability becomes good. For example, it is preferable to use tungsten powders having particle diameter of 5 μm or less and diameter of 27 μm or more.

[0015]

It is also preferable to subject the tungsten powder used in the present invention to a coupling treatment in order to increase its affinity with the resin. Titanate-based, aluminum-based, silane-based coupling agents or the like can be preferably used. In particular, a silane-based coupling agent is preferably used in the present invention, because it improves affinity to the highest extent.

【0016】

It is necessary that the content of the thermoplastic elastomer is 2.5 wt% or more. If the thermoplastic elastomer content in the composition is less than 2.5 wt%, formation of the resin composition is difficult. Even if it can be formed, the moldability of the resin composition is poor.

【0017】

It is preferable that the thermoplastic resin composition of the present invention has a surface hardness of 80 or less, more preferably 60 or less, when measured by the method defined in JIS K-7215 (testing machine type D).

【0018】

It is also necessary that the content of the tungsten powder of 85 wt% or more is necessary. This is because if the content of tungsten powder is less than 85 wt%, the specific gravity of the composition is less than 4.5, which is not sufficient.

【0019】

Therefore, in order to satisfy all of the high specific gravity, a flexibility and a processability (moldability), the contents of the thermoplastic elastomer and the tungsten powder are 2.5 to 15 wt% and 85 to 97.5 wt% respectively.

【0020】

If the thermoplastic resin composition of the present invention is used as a balance weight of a wheel, sports goods or the like, the specific gravity of the thermoplastic resin composition is preferably 8 or more, more preferably 9 or more and even more preferably 10 or more. In order to ensure the above specific gravities, the blending amounts of the tungsten powder are 93.5 wt% or more, 94.5 wt% or more and 95.5 wt% or more respectively. On the other hand, the blending amount of the thermoplastic elastomer necessary to ensure the flexibility required for these applications (as flexible as to be easily bent by hand) is 2.5 wt% or more, preferably 3.0 wt% or more, and even more preferably 4.0 wt%. Therefore, in these applications such as the balance weight, it is necessary to set the blending

amount of the thermoplastic elastomer within the range of 2.5 to 6.5 wt% and the blending amount of the tungsten powder within the range of 93.5 to 97.5 wt%.

【0021】

Furthermore, it is also possible to add to the thermoplastic resin composition of the present invention conventional additives such as antioxidants, thermal stabilizers, ultraviolet absorbers, antistatic agents, crystallization accelerators, coupling agents, lubricants, additive stickers, pigments, dyes, softening agents, anti-aging, crosslinking agents or the like as well as rubber or low molecular weight components, if necessary, within a range that does not inhibit the effect of the present invention.

【0022】

The crosslinking agents are used to crosslink the thermoplastic elastomers, if necessary. The crosslinking agents serve to strengthen the binding among the thermoplastic elastomers and improve resistance against abrasion or damage to a higher extent than compositions with uncrosslinked elastomer. Examples of crosslinking agents include organic peroxides such as 2,5-dimethyl-2,5-t-butylperoxy-3-hexyne, 2,5-dimethyl-2,5-di-t-butylperoxyhexane, di(t-butylperoxy)-m-diisopropylbenzene, di-t-butyl peroxide, dicumyl peroxide, t-butylcumyl peroxide, t-butyl peroxy cumene or the like.

【0023】

The thermoplastic resin composition of the present invention can be manufactured by various kinds of well-known methods such as melt kneading using a single or a double screw extruder, but not limited to those methods. In addition, various kinds of molding processes of the thermoplastic resin composition of the present invention can be employed, such as injection molding and compression molding, but not limited to these processes.

【0024】

Since the thermoplastic resin composition of the present invention is constituted to blend the thermoplastic elastomer having a good

moldability and a flexibility at room temperature and the tungsten powder having a high specific gravity, the thermoplastic resin composition of the present invention has an appropriate flexibility while having a specific gravity as high as or higher than that of lead. In particular, the thermoplastic resin composition of the present invention can be used as a substitute for a balance weight made of toxic lead, and can also be used for various applications such as sports goods, electrical and electronic parts, machine parts and the like.

【0025】

The thermoplastic resin composition of the present invention has excellent moldability and processability because of the use of the thermoplastic elastomer, and it is possible to use various kinds of molding processes including injection molding and compression molding. Furthermore, the used thermoplastic resin composition of the present invention can be recycled by being collected, molten and molded.

【0026】

【Examples】

Hereinafter, the present invention will be described by way of examples. However, the present invention is not limited to these examples. Before referring to the examples, a method for treating tungsten powder with a silane-based coupling agent will be described.

【0027】

(Silane-based coupling method) As the silane-based coupling agent, γ -(2-aminoethyl) aminopropyl trimethoxy silane (SH6020, manufactured by Dow Corning Toray Silicone Co., Ltd.) was used. First, 0.3 wt% of the silane-based coupling agent was dropped into tungsten powder being stirred in a mixer with a high speed stirring blade (super mixer) and the mixture was continuously stirred until the temperature in the mixer reached 120°C. Thereafter, the mixture was cooled and used as a tungsten powder treated with silane-based coupling agent.

【0028】

(Example 1)

As shown in Table 1, 3.0 wt% of a hydrogenated styrene-based thermoplastic elastomer (SEPTON 2063 (manufactured by Kuraray Co., Ltd.), which is a SEPS having a styrene content of 13 wt%, a specific gravity of 0.89, a JIS A hardness of 36, a number-average molecular weight of 1.56E+5 and 4.08 E+4 at two peaks) and 97 wt% of tungsten powder having an average particle diameter of 13 μm (manufactured by Tokyo Tungsten Co., Ltd.) that had been subjected to a coupling treatment were blended and premixed by a mixer with a high speed stirring blade (super mixer). Then, melt-kneading was performed with a single screw extruder having a screw diameter of 25 mm and pellets were obtained. The pellets were heated (80°C) and dried under reduced pressure, and a molded article having a length of 100 mm, a width of 25 mm and a thickness of 2.0 mm was obtained by an injection molding machine. The temperature of the injection molding machine was 240°C and the temperature of the mold was 60°C. The melt flow rate (MFR) of the resin was 2.2 g/10 min. at 230°C and a load of 2.16 kg.

【0029】

(Example 2)

As shown in Table 1, a molded article of the same size was obtained by the same method as in Example 1 except that the pellets were obtained by blending 4.5 wt% of a hydrogenated styrene-based thermoplastic elastomer (SEPTON 4033 (manufactured by Kuraray Co., Ltd.)), which is a SEPS having a styrene content of 30 wt%, a specific gravity of 0.92, a JIS A hardness of 76, a number-average molecular weight of 8.79E+4) and 95.5 wt% of tungsten powder having an average particle diameter of 13 μm (manufactured by Tokyo Tungsten Co., Ltd.) that had been subjected to a coupling treatment and that the temperature for injection molding was 280°C. The MFR of the resin was 0 g/10 min at 230°C and a load of 2.16 kg.

【0030】

(Example 3)

As shown in Table 1, a molded article of the same size was obtained by the same method as in Example 1 except that 14.0 wt% of a hydrogenated styrene-based thermoplastic elastomer (SEPTON 2063 (manufactured by

Kuraray Co., Ltd.)) and 86.0 wt% of tungsten powder having an average particle diameter of 5 μm (manufactured by Tokyo Tungsten Co., Ltd.) that had been subjected to a coupling treatment were blended.

【0031】

(Example 4)

As shown in Table 1, a molded article of the same size by the same method as in Example 3 was obtained except that SEPTON 4033 was used as the thermoplastic elastomer, tungsten powder having an average particle diameter of 3 μm was used and that the temperature for injection molding was 260°C.

【0032】

(Example 5)

A molded article of the same size was obtained by the same method as in Example 1 except that a mixture obtained by blending tungsten powders having an average particle diameter of 5 μm and 27 μm in a blending ratio of 6:4 was used as the tungsten powder.

【0033】

(Comparative Example 1)

As shown in Table 1, 2.0 wt% of a hydrogenated styrene-based thermoplastic elastomer (SEPTON 2063 (manufactured by Kuraray Co., Ltd.)) and 98.0 wt% of tungsten powder having an average particle diameter of 13 μm (manufactured by Tokyo Tungsten Co., Ltd.) that had been subjected to a coupling treatment were blended and premixed in the same manner as in Example 1, and then it was attempted to perform melt-kneading with a single screw extruder. However, the load to the extruder was so large that pellets could not be obtained.

【0034】

(Comparative Example 2)

As shown in Table 1, a molded article of the same size was obtained by the same method as in Example 1 except that 18.0 wt% of a hydrogenated styrene-based thermoplastic elastomer (SEPTON 2063 (manufactured by Kuraray Co., Ltd.)) and 82.0 wt% of tungsten powder having an average

particle diameter of 5 μm (manufactured by Tokyo Tungsten Co., Ltd.) that had been subjected to a coupling treatment were blended.

[0035]

(Comparative Example 3)

As shown in Table 1, a molded article of the same size was obtained by the same method as in Comparative Example 2 except that SEPTON 4033 was used as the thermoplastic elastomer and that the temperature for injection molding was 260°C.

[0036]

(Comparative Example 4)

As shown in Table 1, a molded article of the same size was obtained by the same method as in Example 1 except that 5.7 wt% of Nylon 6 (MC 102 manufactured by Kanebo Gohsen, Ltd.) and 94.3 wt% of tungsten powder having an average particle diameter of 13 μm (manufactured by Tokyo Tungsten Co., Ltd.) that had been subjected to a coupling treatment were blended and that the temperature for injection molding was 260°C.

【0037】

【Table 1】

| | Composition | | | |
|---------------|--|-----------------------|---|-----------------------|
| | Resin component | | Tungsten powder | |
| | type | Blending amount (wt%) | average particle diameter (μm) | blending amount (wt%) |
| Ex. 1 | Thermoplastic elastomer (SEPTON 2063) | 3.0 | 13 | 97.0 |
| Ex. 2 | Thermoplastic elastomer (SEPTON 4033) | 4.5 | 13 | 95.5 |
| Ex. 3 | Thermoplastic elastomer (SEPTON 2063) | 14.0 | 5 | 86.0 |
| Ex. 4 | Thermoplastic elastomer (SEPTON 4033) | 14.0 | 3 | 86.0 |
| Ex. 5 | Thermoplastic elastomer (SEPTON 2063) | 3.0 | 5 | 58.2 |
| | | | 27 | 38.8 |
| Com. Ex. 1 | Thermoplastic elastomer (SEPTON 2063) | 2.0 | 13 | 98.0 |
| Com. Ex. 2 | Thermoplastic elastomer (SEPTON 2063) | 18.0 | 5 | 82.0 |
| Com. Ex. 3 | Thermoplastic elastomer (SEPTON 4033) | 18.0 | 5 | 82.0 |
| Com. Ex. 4 | Thermoplastic plastic (Nylon 6) | 5.7 | 13 | 94.3 |

【0038】

The specific gravity and the surface hardness of the molded articles of Examples 1 to 4 and Comparative Examples 1 to 4 were measured, and the results are shown in Table 2. The measurement of the specific gravity and of the surface hardness was conducted by the method defined in JIS K-7112 and JIS K-7215 (type D of testing machine measuring durometer hardness), respectively.

【0039】

【Table 2】

| | Physical properties | |
|------------|---------------------|------------------|
| | Specific gravity | Surface hardness |
| Ex. 1 | 11.9 | 25 |
| Ex. 2 | 9.9 | 55 |
| Ex. 3 | 5.0 | 8 |
| Ex. 4 | 5.1 | 40 |
| Ex. 5 | 11.9 | 25 |
| Com. Ex. 1 | - | - |
| Com. Ex. 2 | 4.0 | 5 |
| Com. Ex. 3 | 4.2 | 40 |
| Com. Ex. 4 | 10.1 | 90 |

【0040】

As shown in Tables 1 and 2, the molded articles of Examples 1 to 5 having a content of thermoplastic elastomer in the range of 2.5 to 15 wt% and a blending amount of tungsten powder in the range of 85 to 97.5 wt% have a sufficient flexibility (surface hardness of 60 or less) although having a large specific gravity (4.5 or more). On the other hand, in the molded articles of Comparative Examples 2 and 3 containing 18.0 wt% of thermoplastic elastomer and 82.0 wt% of tungsten powder, contents that are outside of the above ranges, a sufficient specific gravity cannot be provided. In the case of Comparative Example 4 where Nylon 6 was used instead of the thermoplastic elastomer, there is the problem that the hardness is too high although the specific gravity is sufficient.

【0041】

Furthermore, the molded articles of Examples 1 and 3 using SEPTON 2063 as the thermoplastic elastomer have a surface hardness of 25 or less and have an excellent flexibility. Therefore, when an excellent flexibility is required, it is preferable to use SEPTON 2063 than SEPTON 4033. That is, it is desirable to use more flexible thermoplastic elastomer.

【0042】

Regarding the tungsten powder, Example 5 containing tungsten powders of a small diameter and a large diameter in combination advantageously has good moldability because the flowability of the resin is excellent although it is equal to Example 1 in the physical properties.

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最終頁に続く

(54)【発明の名称】 热可塑性樹脂組成物

(57)【要約】

【課題】重厚感と柔軟性の双方が要求される種々の物品の形成材料として使用することのできる、高比重で柔軟性があり、加工性に優れた熱可塑性樹脂組成物を提供する。

【解決手段】ステレン系熱可塑性エラストマー2.5~15重量%と、平均粒子径13μmのタンゲステン粉末8.5~97.5重量%とを配合し、高速搅拌撹付混合槽(スーパーミキサー)で予備混合した後、スクリュー径が25mmの単軸押出機で溶融混練して得られた熱可塑性樹脂組成物。

【0006】そこで、この発明の課題は、高分子材料である熱可塑性樹脂を使用することで、上述したバランスウエイト等のように、重量感と柔軟性の双方が要求される種々の物品の形成材料として使用することのできる、鉛に匹敵する高比重でありながら、しかも高度の柔軟性があり、加工性に極めて優れた熱可塑性樹脂組成物を提供することにある。

【0007】

【課題を解決するための手段及びその効果】上記の課題を解決するため、この発明は、熱可塑性エラストマー2、5～15重量%と、タングステン粉末85～97.5重量%を含有することを特徴とする熱可塑性樹脂組成物。

10 【請求項1】 前記熱可塑性エラストマーが、ステレン系熱可塑性エラストマーである請求項1に記載の熱可塑性樹脂組成物。

【請求項2】 前記熱可塑性エラストマーが、ポリスチレン-ボリイソブレンブロック共重合体の水素添加物またはポリスチレン-ボリブタジエンブロック共重合体の水素添加物またはポリスチレン-ボリイソブレンブロック共重合体のイソブレン部にブタジエンユニットを含むものの水素添加物またはこれらの混合物である請求項2に記載の熱可塑性樹脂組成物。

【請求項3】 JIS K-7215に規定された方法によって測定された表面硬度が80以下である請求項1、2または3に記載の熱可塑性樹脂組成物。

【請求項4】 比重が8以上である請求項1、2、3または4に記載の熱可塑性樹脂組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、高比重で、柔軟性に優れた熱可塑性樹脂組成物に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】高分子材料は、金属材料に比べて加工が容易で耐蝕性に優れ、かつ軽量である上に比較的安価なこと、絶縁性が良好であること等の理由から、近年電気・電子部品、機械部品、精密部品、一般工業部品などの素材や構造材料として、多くの分野において幅広く用いられている。

【0003】また、高分子材料は、切削加工や焼結工程等を必要とする金属材料に比べて加工性に優れており、特に、射出成形法を採用した場合には、複雑な形状の成形品が一工程で成形できるという利点がある。

【0004】ところで、自動車等のホイールバランスを調整するためにホイールに装着されるバランスウエイトは、ホイールの外観を損なわないように極力小さい方がよく、ホイールのリム径に合わせることができるように容易に変形することが望ましい等の理由で、従来から、高比重で、柔軟性を備えた金属材料である鉛がバランスウエイトの形成材料として使用されてきた。

【0005】しかしながら、鉛には毒性があり、しかも、皮膚から人間の体内に侵入した鉛は骨に沈着すると極めて排出されにくく、人間の体内に蓄積されることとなる。そして、万一人間の体内に鉛が蓄積されると、鉛中毒を起こす可能性も皆無ではないので、上述したようなホイールのバランスウエイト等についても、鉛以外の材料によって形成することが望まれているが、鉛のように高比重で適度な柔軟性を備えた材料は存在していないのが現状である。

【0006】そこで、この発明の課題は、高分子材料である熱可塑性樹脂を使用することで、上述したバランスウエイト等のように、重量感と柔軟性の双方が要求される種々の物品の形成材料として使用することのできる、鉛に匹敵する高比重でありながら、しかも高度の柔軟性があり、加工性に極めて優れた熱可塑性樹脂組成物を提供することにある。

【0007】

【課題を解決するための手段及びその効果】上記の課題を解決するため、この発明は、熱可塑性エラストマー2、5～15重量%と、タングステン粉末85～97.5重量%をブレンドすることにより、高比重で柔軟性があり、加工性に優れた熱可塑性樹脂組成物を提供するものである。

【0008】本発明に用いられる熱可塑性エラストマーは、分子中に弾性を持つゴム成分（ソフトセグメント）と、塑性変形を防止するための分子拘束成分（ハードセグメント）との両成分を持っており、ソフトセグメントの分子運動が局所的にハードセグメントによって拘束されているため、常温ではゴム弾性体としての挙動をとるが、温度上昇によって塑性変形をする高分子材料のことである。高温で可塑化して成形が可能となり、常温下ではその形状を保ち、かつ容易に変形することが求められるためである。

【0009】具体的には、ハードセグメントがポリスチレン、ソフトセグメントが（水添）ポリブタジエンや（水添）ポリイソブレンであるステレン系熱可塑性エラストマー、ハードセグメントがポリエチレンやポリプロピレン、ソフトセグメントがエチレン・プロピレン・ジエン共重合体（EPM）やブチルゴムであるオレフィン系熱可塑性エラストマー、ハードセグメントがポリエチテル、ソフトセグメントがポリエーテルや脂肪族ポリエチテルであるポリエチテル系熱可塑性エラストマー、ハードセグメントがウレタン構造、ソフトセグメントがポリエーテルやポリエチテルであるウレタン系熱可塑性エラストマー、ハードセグメントがポリアミド、ソフトセグメントがポリエーテルやポリエチテルであるポリアミド系熱可塑性エラストマーが挙げられる。

【0010】また、ハードセグメントがシンジオタクチック1,2-ボリブタジエン、ソフトセグメントが非結晶ポリブタジエンである1,2-ボリブタジエン系熱可塑性エラストマー、ハードセグメントがトランス1,4-ポリイソブレン、ソフトセグメントが非結晶ポリイソブレンであるトランス1,4-ポリイソブレン系熱可塑性エラストマー、ハードセグメントが金属カルボキシレートイオンクラスター、ソフトセグメントが非結晶ポリエチレンであるアイオノマー、ハードセグメントが結晶ポリエチレン、ソフトセグメントがエチレン-エチルアクリレート共重合体またはエチレン-酢酸ビニル共重合体であるPE/EVA系熱可塑性エラストマ

一、ハードセグメントがフッ素系樹脂、ソフトセグメントがフッ素系ゴムであるフッ素系熱可塑性エラストマー等を使用することも可能である。

【0011】また、使用する熱可塑性エラストマーは、屋外での使用を考慮すると、耐候性、耐老化性に優れている必要があり、例えば、100℃程度まで上昇する自動車のホイールに装着されるバランスウエイトとして使用されるような場合には、100℃程度の温度で溶融しないような耐熱性がさらに要求されることになる。こういった要求を満足するためには、使用する熱可塑性エラストマーが二重結合を持たず、加水分解等を起こさないものであることが望ましく、具体的には、中間のソフトセグメントを構成するポリイソブレン部分やポリブタジエン部分を、水素添加して飽和したステレン系熱可塑性エラストマーの水素添加物(SEPS、SEBS)等が適している。なお、中間のイソブレン部分にブタジエンのユニットを含むステレン系熱可塑性エラストマーの水素添加物を用いることも可能であり、SEPS、SEBS等、種類の異なる2種類以上のステレン系熱可塑性エラストマーの水素添加物を混合したものであってもよい。

【0012】例えば、上述したSEPSの場合、ステレンの含量、イソブレンの分子量、分子量分布等によって物性が変化する。即ち、ステレン含量が増えるほど硬くなり、イソブレンの分子量が大きくなるほど強度が大きくなる。また、分子量分布がシャープになるほど成形性が低下し、特に、イソブレンの分子量が大きく、その分子量分布がシャープであると、成形が極めて困難となる。ステレンの含量については10～65%程度のものが一般的に知られているが、本発明で使用するSEPSとして適しているのは、ステレン含量が13～30%、好ましくは13～20%程度のものである。また、SEPS自身の成形性については、230℃、2.16kgの条件でのMFRが0.05g/10分以上、好ましくは0.5g/10分以上、さらに好ましくは1g/10分以上のものであるのがよい。これは、タンクスチン粉末をブレンドすることにより、熱可塑性エラストマー単独の場合に比べて成形性が低下するからである。

【0013】こういったステレン系熱可塑性エラストマーは、アルキルリチウム等の一官能性開始剤を用いて、40ステレン-イソブレン-ステレン、ステレン-ブタジエン-ステレンの順序でリビング重合してブロック共重合体を製造(一官能性開始剤による三段階重合)し、水素添加する方法や、同様の開始剤を用いて同様にリビング重合した後、ジハロゲン化アルキルでカップリングして、ブロック共重合体を製造(二段階重合カップリング法)し、水素添加する方法等によって製造することができる。なお、本発明で使用する熱可塑性エラストマーはペレット状でもパウダー状でもよい。

【0014】本発明に使用するタンクスチンは、熱可塑

性エラストマーと均一にブレンドする必要があることから、粉末状であることが望ましく、その粒子径は好ましくは300μm以下、より好ましくは2～100μm、さらに好ましくは3～30μm、特に好ましくは3～27μmである。タンクスチン粉末の粒子径が大きくなると、射出成形法等を採用して成形する場合に、熱可塑性樹脂組成物が企型のゲートを通過しにくくなり、成形性が低下するからである。また、粒子径が極端に小さくなると、タンクスチン粉末の表面積が大きくなり、所定量の熱可塑性エラストマーによってタンクスチン粉末の表面を完全に被うことができなくなるからである。なお、粒子径が小さいものと大きいものを併用すると、樹脂組成物の流动性が向上し、成形性が良好となるため好ましく、例えば、5μm以下のものと、27μm以上のものを用いることが好ましい。

【0015】また、本発明で使用するタンクスチン粉末は、樹脂との親和性を高める場合には、カップリング処理をして用いることが好ましい。カップリング剤としては、チタネート系、アルミニウム系、シラン系等が用いられるが、本発明においては、シラン系が最も親和性改善効果が高い。

【0016】本発明に用いる熱可塑性エラストマーの配合量は、2.5重量%以上であることが肝要である。熱可塑性エラストマーの配合量が2.5重量%未満であれば、樹脂の形成が困難となる。また、仮に成形できるとしても成形性が悪いものとなるからである。

【0017】なお、本発明の熱可塑性樹脂組成物は、JIS K-7215(試験機タイプD)に規定された方法によって測定された表面硬度が80以下であることが好ましく、さらに好ましくは60以下である。

【0018】また、本発明に用いるタンクスチン粉末の配合量は、8.5重量%以上であることが肝要である。タンクスチン粉末の配合量が8.5重量%未満の場合、比重が4.5未満となって十分な比重を確保することができないからである。

【0019】従って、高比重、柔軟性及び加工性(成形性)の全てを満足させるためには、使用する熱可塑性エラストマーの配合量及びタンクスチン粉末の配合量は、それぞれ2.5～1.5重量%、8.5～97.5重量%となる。

【0020】なお、ホイールのバランスウエイトやスポーツ用具等として使用する場合は、比重が好ましくは8以上、さらに好ましくは9以上、特に好ましくは10以上であり、この比重を確保するためのタンクスチン粉末の配合量は、それぞれ9.3.5重量%以上、9.4.5重量%以上、9.5.5重量%以上である。一方、これらの用途に用いる場合に要求される柔軟性(手で容易に曲げることができる程度)を確保するために必要なステレン系熱可塑性エラストマーの配合量は、2.5重量%以上、好ましくは3.0重量%以上、さらに好ましくは

本発明はこれらの実施例に限定されるものではない。なお、実施例に先立って、タンクスチン粉末のシラン系カップリング処理方法について説明する。

【0027】(シラン系カップリング処理方法) シラン系カップリング剤として、アーティカル(2-アミノエチル)アミノプロピルトリメトキシシラン(SH6020、東レ・ダウコーニング・シリコーン(株)製)を使用した。高速搅拌翼付き混合槽(スーパーミキサー)で搅拌中のタンクスチン粉末へ、シラン系カップリング剤を0.3重量%滴下し、槽内温度が120℃になるまで搅拌を続けた。その後冷却し、シラン系カップリング処理済みタンクスチン粉末として使用した。

【0028】(実施例1) 表1に示すように、ステレン系熱可塑性エラストマーの水素添加物(セブトン2063(クラレ製)、ステレン含有量が13重量%のS E P S、比重: 0.89、JIS A硬度36、数平均分子量は 1.56×10^5 及び 4.08×10^4 の2ピーク)3.0重量%、事前にシラン系カップリング処理を行った平均粒子径 $1.3 \mu\text{m}$ のタンクスチン粉末(東京タンクスチン製)9.7重量%を配合し、高速搅拌翼付き混合槽(スーパーミキサー)で予備混合した後、スクリュー径が25mmの単軸押出機で溶融混練してペレットを得た。このペレットを減圧下で加热(80℃)乾燥し、射出成形機によって、長さ100mm、幅25mm、厚み2.0mmの成形品を得た。なお、射出成形機の温度は240℃、成型温度は60℃とした。また、本樹脂の230℃、荷重2.16kgでのマルトフローレート(M F R)は、2.2g/10分であった。

【0029】(実施例2) 表1に示すように、ステレン系熱可塑性エラストマーの水素添加物(セブトン4033(クラレ製)、ステレン含有量が30重量%のS E P S、比重: 0.92、JIS A硬度76、数平均分子量 8.79×10^4 、5重量%、事前にシラン系カップリング処理を行った平均粒子径 $1.3 \mu\text{m}$ のタンクスチン粉末(東京タンクスチン製)9.5:5重量%を配合し、射出成形温度を280℃とする他は、実施例1と同様の方法により、同一サイズの成形品を得た。なお、本樹脂の230℃、荷重2.16kgでのM F Rは0g/10分であった。

【0030】(実施例3) 表1に示すように、ステレン系熱可塑性エラストマーの水素添加物(セブトン2063(クラレ製))14.0重量%、事前にシラン系カップリング処理を行った平均粒子径 $5 \mu\text{m}$ のタンクスチン粉末(東京タンクスチン製)86.0重量%を配合し、実施例1と同様の方法により、同一サイズの成形品を得た。

【0031】(実施例4) 表1に示すように、熱可塑性エラストマーとしてセブトン4033を使用すると共に平均粒子径が $3 \mu\text{m}$ のタンクスチン粉末を使用し、射出成形温度を260℃とする他は、実施例3と同様の方法

4. 0重量%以上である。従って、こういったバランスウエイト等の用途に使用する場合は、結局、ステレン系熱可塑性エラストマーの配合量が2.5~6.5重量%、タンクスチン粉末の配合量が93.5~97.5重量%の範囲内にそれぞれ入るように設定しておく必要がある。

【0021】なお、本発明の熱可塑性樹脂組成物には、本発明の目的を損なわない範囲で、必要に応じてゴムや低分子量成分の他、通常の添加剤、例えば、酸化防止剤、熱安定剤、紫外線吸収剤、帶電防止剤、結晶化促進剤、カップリング剤、骨材、添加剤添着液、顔料、染料、軟化剤、老化防止剤、架橋剤等を添加することができる。

【0022】前記架橋剤は、必要に応じて熱可塑性エラストマーを架橋するために使用するものであり、熱可塑性エラストマー間の結びつきを強化し、こすれや破壊に対して未架橋のものより抵抗力を高める働きをする。架橋剤としては、例えば、2,5-ジメチル-2,5-t-ブチルバーオキシルヘキシン-3、2,5-ジメチル-2,5-ジ-t-ブチルバーオキシヘキサン、ジ(t-ブチルバーオキシ)-m-ジイソプロピルベンゼン、ジ-t-ブチルバーオキサイド、ジクミルバーオキサイド、t-ブチルクミルバーオキサイド、t-ブチルバーオキシクメン等の有機過酸化物を使用することができる。

【0023】本発明の熱可塑性樹脂組成物の製造方法は、特に限定されるものではなく、単軸または2軸押出機を用いて、タンクスチン粉末と熱可塑性エラストマーとを溶融混練する方法等、公知の種々の方法を採用することができる。また、本発明の熱可塑性樹脂組成物の成形方法についても、特に限定されるものではなく、例えば、射出成形法、圧縮成形法等、公知の種々の方法を採用することができる。

【0024】以上のように、本発明の熱可塑性樹脂組成物は、成形しやすく、常温において柔軟性を有する熱可塑性エラストマーと高比重のタンクスチン粉末とをブレンドする構成を採用したため、鉛と同等もしくはそれ以上の高比重でありながら、しかも適度な柔軟性が確保されることになり、特に、毒性のある鉛製のバランスウエイトの代替物として使用することができるほか、種々のスポーツ用具、電気・電子部品、機械部品等、様々な用途に使用することができる。

【0025】また、本発明の熱可塑性樹脂組成物は、熱可塑性エラストマーを使用していることから、射出成形法や圧縮成形法等の種々の成形法を採用することができ、成形性、加工性に極めて優れていると共に、使用済みの同材料を溶融、成形することにより再生するといったリサイクルが可能であるという利点がある。

【0026】

【実施例】以下、本発明の実施例について説明するが、

により、同一サイズの成形品を得た。

【0032】(実施例5) タングステン粉末として、平均粒子径 $5\text{ }\mu\text{m}$ と $27\text{ }\mu\text{m}$ のものを、6:1の割合に混合したものを用いる他は、実施例1と同様の方法により、同一サイズの成形品を得た。

【0033】(比較例1) 表1に示すように、スチレン系熱可塑性エラストマーの水素添加物(セブトン2063(クラレ製))2.0重量%、事前にシラン系カップリング処理を行った平均粒子径 $13\text{ }\mu\text{m}$ のタングステン粉末(東京タングステン製)98.0重量%を配合し、実施例1と同様に、予備混合した後に、単軸押出機で溶融混練しようとしたが、押出機の負荷が大きく、ペレットを採取することができなかつた。

【0034】(比較例2) 表1に示すように、スチレン系熱可塑性エラストマーの水素添加物(セブトン2063(クラレ製))18.0重量%、事前にシラン系カップリング処理を行った平均粒子径 $5\text{ }\mu\text{m}$ のタングステン

粉末(東京タングステン製)82.0重量%を配合し、実施例1と同様の方法により同一サイズの成形品を得た。

【0035】(比較例3) 表1に示すように、熱可塑性エラストマーとしてセブトン4033を使用し、射出成形温度を 260°C とする他は、比較例2と同様の方法により、同一サイズの成形品を得た。

【0036】(比較例4) 表1に示すように、ナイロン6(MC102カネボウ合纏(株)製)5.7重量%、事前にシラン系カップリング処理を行った平均粒子径 $13\text{ }\mu\text{m}$ のタングステン粉末(東京タングステン製)94.3重量%を配合し、射出成形温度を 260°C とする他は、実施例1と同様の方法により同一サイズの成形品を得た。

【0037】

【表1】

| 種類 | 組成 | | |
|------|----------------------|--------------|----------------------------|
| | 樹脂成分 | タンクステン粉末 | |
| | | 配合量 [重量%] | 平均粒子径 [μm] |
| 実施例1 | 熱可塑性エラストマー(セブトン2063) | 3.0 | 13 |
| 実施例2 | 熱可塑性エラストマー(セブトン4033) | 4.5 | 13 |
| 実施例3 | 熱可塑性エラストマー(セブトン2063) | 14.0 | 5 |
| 実施例4 | 熱可塑性エラストマー(セブトン4033) | 14.0 | 3 |
| 実施例5 | 熱可塑性エラストマー(セブトン2063) | 3.0 | 5 27 |
| 比較例1 | 熱可塑性エラストマー(セブトン2063) | 2.0 | 13 |
| 比較例2 | 熱可塑性エラストマー(セブトン2063) | 18.0 | 5 |
| 比較例3 | 熱可塑性エラストマー(セブトン4033) | 18.0 | 5 |
| 比較例4 | 熱可塑性プラスチック(ナイロン6) | 5.7 | 13 |
| | | | 94.3 |

【0038】上述した実施例1~4及び比較例1~4の各成形品について、それぞれ比重及び表面硬度を測定し、その結果を表2に示した。なお、比重はJIS K-7112、表面硬度はJIS K-7215(デュロメータ硬さを測定する試験機のタイプD)にそれぞれ50

規定する方法に基づいて測定した。

【0039】

【表2】

| | 物 性 | |
|------|--------|------|
| | 比重 | 表面硬度 |
| 実施例1 | 11.9 | 25 |
| 実施例2 | 9.9 | 55 |
| 実施例3 | 5.0 | 8 |
| 実施例4 | 5.1 | 40 |
| 実施例5 | 11.9 | 25 |
| 比較例1 | - | - |
| 比較例2 | 4.0 | 5 |
| 比較例3 | 4.2 | 40 |
| 比較例4 | 10.1 | 90 |

【0040】表1及び表2に示すように、熱可塑性エラストマーの配合量が2.5～15重量%、タンクスチーン粉末の配合量が8.5～9.7.5重量%の範囲内にある実施例1～5は、比重が大きい(4.5以上)にも拘わらず十分な柔軟性(表面硬度が60以下)を備えているの

に対して、熱可塑性エラストマーの配合量が18.0重量%、タンクスチーン粉末の配合量が82.0重量%と、上述した範囲外にある比較例2、3については、4.5以上の十分な比重を確保することができないことが分かる。また、熱可塑性エラストマーの代わりにナイロン6を使用した比較例4は、比重は十分である一方、硬度が高すぎるという問題を有していた。

【0041】さらに、熱可塑性エラストマーとしてセプトン2063を使用した実施例1、3では、表面硬度が25以下となり、優れた柔軟性が得られることが分かる。従って、優れた柔軟性を要求される場合は、セプトン4033を使用するよりもセプトン2063を使用するほうが望ましい。即ち、元々の熱可塑性エラストマーが柔軟なものを使用するのが望ましい。

【0042】また、タンクスチーン粉末として、粒子径が小さいものと大きいものを併用した実施例5は、物性面において実施例1と同等であったが、樹脂の流动性が優れているため、成形性が良いという利点を有していた。

フロントページの続き

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Fターム(参考) 4J002 BP011 DA116 FB096 FD016

claimed genus prior to the reference's or activity's date. The test is whether the species completed by applicant prior to the reference date or the activity's date provided an adequate basis for inferring that the invention has generic applicability. *In re Plumb*, 470 F.2d 1403, 176 USPQ 323 (CCPA 1973); *In re Rainer*, 390 F.2d 771, 156 USPQ 334 (CCPA 1968); *In re Clarke*, 356 F.2d 987, 148 USPQ 665 (CCPA 1966); *In re Shokal*, 242 F.2d 771, 113 USPQ-283 (CCPA 1957).

It is not necessary for the affidavit evidence to show that the applicant viewed his or her invention as encompassing more than the species actually made. The test is whether the facts set out in the affidavit are such as would persuade one skilled in the art that the applicant possessed so much of the invention as is shown in the reference or activity. *In re Schaub*, 537 F.2d 509, 190 USPQ 324 (CCPA 1976).

C. Species Versus Embodiments

References or activities which disclose one or more embodiments of a single claimed invention, as opposed to species of a claimed genus, can be overcome by filing a 37 CFR 1.131 affidavit showing prior completion of a single embodiment of the invention, whether it is the same or a different embodiment from that disclosed in the reference or activity. See *In re Fong*, 288 F.2d 932, 129 USPQ 264 (CCPA 1961) (Where applicant discloses and claims a washing solution comprising a detergent and polyvinylpyrrolidone (PVP), with no criticality alleged as to the particular detergent used, the PVP being used as a soil-suspending agent to prevent the redeposition of the soil removed, the invention was viewed as the use of PVP as a soil-suspending agent in washing with a detergent. The disclosure in the reference of the use of PVP with two detergents, both of which differed from that shown in applicant's 37 CFR 1.131 affidavit, was considered a disclosure of different embodiments of a single invention, rather than species of a claimed genus); *In re Defano*, 392 F.2d 280, 157 USPQ 192 (CCPA 1968).

REFERENCE OR ACTIVITY DISCLOSES CLAIMED GENUS

In general, where the reference or activity discloses the claimed genus, a showing of completion of a single species within the genus is sufficient to antedate

the reference or activity under 37 CFR 1.131. *Ex parte Biesecker*, 144 USPQ 129 (Bd. App. 1964).

In cases where predictability is in question, on the other hand, a showing of prior completion of one or a few species within the disclosed genus is generally not sufficient to overcome the reference or activity. *In re Shokal*, 242 F.2d 771, 113 USPQ 283 (CCPA 1957). The test is whether the species completed by applicant prior to the reference date or the date of the activity provided an adequate basis for inferring that the invention has generic applicability. *In re Mantell*, 454 F.2d 1398, 172 USPQ 530 (CCPA 1973); *In re Rainer*, 390 F.2d 771, 156 USPQ 334 (CCPA 1968); *In re DeFano*, 392 F.2d 280, 157 USPQ 192 (CCPA 1968); *In re Clarke*, 356 F.2d 987, 148 USPQ 665 (CCPA 1965). In the case of a small genus such as the halogens, which consists of four species, a reduction to practice of three, or perhaps even two, species might show possession of the generic invention, while in the case of a genus comprising hundreds of species, reduction to practice of a considerably larger number of species would be necessary. *In re Shokal, supra*.

It is not necessary for the affidavit evidence to show that the applicant viewed his or her invention as encompassing more than the species he or she actually made. The test is whether the facts set out in the affidavit are such as would persuade one skilled in the art that the applicant possessed so much of the invention as is shown in the reference. *In re Schaub*, 537 F.2d 509, 190 USPQ 324 (CCPA 1976).

715.04 Who May Make Affidavit or Declaration; Formal Requirements of Affidavits and Declarations

WHO MAY MAKE AFFIDAVIT OR DECLARATION

The following parties may make an affidavit or declaration under 37 CFR 1.131:

(A) All the inventors of the subject matter claimed:

(B) An affidavit or declaration by less than all named inventors of an application is accepted where it is shown that less than all named inventors of an application invented the subject matter of the claim or claims under rejection. For example, one of two joint

inventors is accepted where it is shown that one of the joint inventors is the sole inventor of the claim or claims under rejection.

(C) A party qualified under 37 CFR 1.42, 1.43, or 1.47 in situation where some or all of the inventors are not available or not capable of joining in the filing of the application.

(D) The assignee or other party in interest when it is not possible to produce the affidavit or declaration of the inventor. *Ex parte Foster*, 1903 C.D. 213, 105 O.G. 261 (Comm'r Pat. 1903).

Affidavits or declarations to overcome a rejection of a claim or claims must be made by the inventor or inventors of the subject matter of the rejected claim(s), a party qualified under 37 CFR 1.42, 1.43, or 1.47, or the assignee or other party in interest when it is not possible to produce the affidavit or declaration of the inventor(s). Thus, where all of the named inventors of a pending application are not inventors of every claim of the application, any affidavit under 37 CFR 1.131 could be signed by only the inventor(s) of the subject matter of the rejected claims. Further, where it is shown that a joint inventor is deceased, refuses to sign, or is otherwise unavailable, the signatures of the remaining joint inventors are sufficient. However, the affidavit or declaration, even though signed by fewer than all the joint inventors, must show completion of the invention by all of the joint inventors of the subject matter of the claim(s) under rejection. *In re Carlson*, 79 F.2d 900, 27 USPQ 400 (CCPA 1935).¹

FORMAL REQUIREMENTS OF AFFIDAVITS AND DECLARATIONS

An affidavit is a statement in writing made under oath before a notary public, magistrate, or officer authorized to administer oaths. See MPEP § 604 through § 604.06 for additional information regarding formal requirements of affidavits.

37 CFR 1.68 permits a declaration to be used instead of an affidavit. The declaration must include an acknowledgment by the declarant that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. 1001) and may jeopardize the validity of the application or any patent issuing thereon. The declarant must set forth in the body of the declaration that all statements made of the declarant's own knowledge are true and that all state-

ments made on information and belief are believed to be true.

715.05 U.S. Patent or Application Publication Claiming Same Invention

When the reference in question is a noncommonly owned U.S. patent or patent application publication claiming the same invention as applicant and its publication date is less than 1 year prior to the presentation of claims to that invention in the application being examined, applicant's remedy, if any, must be by way of 37 CFR 1.608 instead of 37 CFR 1.131. If the reference is claiming the same invention as the application and its publication date is less than 1 year prior to the presentation of claims to that invention in the application, this fact should be noted in the Office action. The reference can then be overcome only by way of interference. See MPEP §§ 2306-2308. If the reference is claiming the same invention as the application and its publication date is 1 year or more prior to the presentation of claims to that invention in the application, a rejection of the claims of the application under 35 U.S.C. 135(b) should be made. See *In re McGrew*, 120 F.3d 1236, 1238, 43 USPQ2d 1632, 1635 (Fed. Cir. 1997) (The court holding that application of 35 U.S.C. 135(b) is not limited to *inter partes* interference proceedings, but may be used as a basis for *ex parte* rejections.).

Form paragraph 23.14 or 23.14.01 may be used when making a rejection under 35 U.S.C. 135(b).

¶ 23.14 Claims Not Copied Within One Year of Patent Issue Date

Claim [1] rejected under 35 U.S.C. 135(b) as not being made prior to one year from the date on which U.S. Patent No. [2] was granted. See *In re McGrew*, 120 F.3d 1236, 1238, 43 USPQ2d 1632, 1635 (Fed. Cir. 1997) where the Court held that the application of 35 U.S.C. 135(b) is not limited to *inter partes* interference proceedings, but may be used as a basis for *ex parte* rejections.

¶ 23.14.01 Claims Not Copied Within One Year of Application Publication Date

Claim [1] rejected under 35 U.S.C. 135(b) as not being made prior to one year from the date on which [2] was published under 35 U.S.C. 122(b). See *In re McGrew*, 120 F.3d 1236, 1238, 43 USPQ2d 1632, 1635 (Fed. Cir. 1997) where the Court held that the application of 35 U.S.C. 135(b) is not limited to *inter partes* interference proceedings, but may be used as a basis for *ex parte* rejections.

Examiner Note:

or declaration do not require corroboration; an applicant may stand on his or her own affidavit or declaration if he or she so elects. *Ex parte Hook*, 102 USPQ 130 (Bd. App. 1953).

Form paragraph 7.59 or 7.63 (both reproduced in MPEP § 715) may be used where insufficient evidence is included in a 37 CFR 1.131 affidavit.

715.07(a) Diligence

Where conception occurs prior to the date of the reference, but reduction to practice is afterward, it is not enough merely to allege that applicant or patent owner had been diligent. *Ex parte Hunter*, 1889 C.D. 218, 49 O.G. 733 (Comm'r Pat. 1889). Rather, applicant must show evidence of facts establishing diligence.

In determining the sufficiency of a 37 CFR 1.131 affidavit or declaration, diligence need not be considered unless conception of the invention prior to the effective date is clearly established, since diligence comes into question only after prior conception is established. *Ex parte Kantor*, 177 USPQ 455 (Bd. App. 1958).

What is meant by diligence is brought out in *Christie v. Seybold*, 1893 C.D. 515, 64 O.G. 1650 (6th Cir. 1893). In patent law, an inventor is either diligent at a given time or he is not diligent; there are no degrees of diligence. An applicant may be diligent within the meaning of the patent law when he or she is doing nothing, if his or her lack of activity is excused. Note, however, that the record must set forth an explanation or excuse for the inactivity; the USPTO or courts will not speculate on possible explanations for delay or inactivity. See *In re Nelson*, 420 F.2d 1079, 164 USPQ 458 (CCPA 1970). Diligence must be judged on the basis of the particular facts in each case. See MPEP § 2138.06 for a detailed discussion of the diligence requirement for proving prior invention.

Under 37 CFR 1.131, the critical period in which diligence must be shown begins just prior to the effective date of the reference or activity and ends with the date of a reduction to practice, either actual or constructive (i.e., filing a United States patent application). Note, therefore, that only diligence before reduction to practice is a material consideration. The "lapse of time between the completion or reduction to practice of an invention and the filing of an application thereon" is not relevant to an affidavit or declara-

tion under 37 CFR 1.131. See *Ex parte Merz*, 75 USPQ 296 (Bd. App. 1947).

Form paragraph 7.62 (reproduced in MPEP § 715) may be used to respond to a 37 CFR 1.131 affidavit where diligence is lacking.

715.07(b) Interference Testimony Sometimes Used

In place of an affidavit or declaration the testimony of the applicant in an interference may be sometimes used to antedate a reference in lieu of 37 CFR 1.131 affidavit or declaration.

The part of the testimony to form the basis of priority over the reference should be pointed out. *Ex parte Bowyer*, 1939 C.D. 5, 42 USPQ 526 (Comm'r Pat. 1939).

715.07(c) Acts Relied Upon Must Have Been Carried Out in This Country or a NAFTA or WTO Member Country

35 U.S.C. 104. Invention Made Abroad.

(a) IN GENERAL.—

(1) PROCEEDINGS.—In proceedings in the Patent and Trademark Office, in the courts, and before any other competent authority, an applicant for a patent, or a patentee, may not establish a date of invention by reference to knowledge or use thereof, or other activity with respect thereto, in a foreign country other than a NAFTA country or a WTO member country, except as provided in sections 119 and 365 of this title.

(2) RIGHTS.—If an invention was made by a person, civil or military—

(A) while domiciled in the United States, and serving in any other country in connection with operations by or on behalf of the United States,

(B) while domiciled in a NAFTA country and serving in another country in connection with operations by or on behalf of that NAFTA country, or

(C) while domiciled in a WTO member country and serving in another country in connection with operations by or on behalf of that WTO member country, that person shall be entitled to the same rights of priority in the United States with respect to such invention as if such invention had been made in the United States, that NAFTA country, or that WTO member country, as the case may be.

(3) USE OF INFORMATION.—To the extent that any information in a NAFTA country or a WTO member country concerning knowledge, use, or other activity relevant to proving or disproving a date of invention has not been made available for use in a proceeding in the Patent and Trademark Office, a court, or any other competent authority to the same extent as such information could be made available in the United States, the Director,

court, or such other authority shall draw appropriate inferences, or take other action permitted by statute, rule, or regulation, in favor of the party that requested the information in the proceeding.

(b) DEFINITIONS.—As used in this section—

(1) The term "NAFTA country" has the meaning given that term in section 2(4) of the North American Free Trade Agreement Implementation Act; and

(2) The term "WTO member country" has the meaning given that term in section 2(10) of the Uruguay Round Agreements Act.

The 37 CFR 1.131 affidavit or declaration must contain an allegation that the acts relied upon to establish the date prior to the reference or activity were carried out in this country or in a NAFTA country or WTO member country. See 35 U.S.C. 104.

Under 37 CFR 1.131(a), which provides for the establishment of a date of completion of the invention in a NAFTA or WTO member country, as well as in the United States, an applicant can establish a date of completion in a NAFTA member country on or after December 8, 1993, the effective date of section 331 of Public Law 103-182, the North American Free Trade Agreement Act, and can establish a date of completion in a WTO member country other than a NAFTA member country on or after January 1, 1996, the effective date of section 531 of Public Law 103-465, the Uruguay Round Agreements Act. Acts occurring prior to the effective dates of NAFTA or URAA may be relied upon to show completion of the invention; however, a date of completion of the invention may not be established under 37 CFR 1.131 before December 8, 1993 in a NAFTA country or before January 1, 1996 in a WTO country other than a NAFTA country.

715.07(d) Disposition of Exhibits

Exhibits, such as those filed as part of an affidavit or declaration under 37 CFR 1.131, must comply with the requirements of 37 CFR 1.91 to be entered into an application file. Exhibits that do not comply with the requirements of 37 CFR 1.91 will be disposed of or returned to applicant at the discretion of the Office. See also MPEP § 608.03(a).

715.08 Passed Upon by Primary Examiner

The question of sufficiency of affidavits or declarations under 37 CFR 1.131 should be reviewed and decided by a primary examiner.

Review of questions of formal sufficiency and propriety are by petition. Such petitions are answered by the Technology Center Directors (MPEP § 1002.02(c)).

Review on the merits of a 37 CFR 1.131 affidavit or declaration is by appeal to the Board of Patent Appeals and Interferences.

715.09 Seasonable Presentation

Affidavits or declarations under 37 CFR 1.131 must be timely presented in order to be admitted. Affidavits and declarations submitted under 37 CFR 1.131 and other evidence traversing rejections are considered timely if submitted:

- (A) prior to a final rejection;
- (B) before appeal in an application not having a final rejection; or
- (C) after final rejection and submitted
 - (1) with a first reply after final rejection for the purpose of overcoming a new ground of rejection or requirement made in the final rejection, or
 - (2) with a satisfactory showing under 37 CFR 1.116(b) or 37 CFR 1.195, or
 - (3) under 37 CFR 1.129(a).

All admitted affidavits and declarations are acknowledged and commented upon by the examiner in his or her next succeeding action.

For affidavits or declarations under 37 CFR 1.131 filed after appeal, see 37 CFR 1.195 and MPEP § 1211.02.

Review of an examiner's refusal to enter an affidavit as untimely is by petition and not by appeal to the Board of Patent Appeals and Interferences. *In re Deters*, 515 F.2d 1152, 185 USPQ 644 (CCPA 1975); *Ex parte Hale*, 49 USPQ 209 (Bd. App. 1941). See MPEP § 715.08 regarding review of questions of propriety of 37 CFR 1.131 affidavits and declarations.

715.10 Review of Affidavit or Declaration for Evidence of Prior Public Use or Sale or Failure to Disclose Best Mode

Any affidavits or declarations submitted under 37 CFR 1.131 and the accompanying evidence must be reviewed carefully by the examiner in order to determine whether they show that the claimed invention



PATENT APPLICATION

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicants: Tetsuo NISHIKAWA et al

For: THERMOPLASTIC RESIN COMPOSITION

Serial No.: 09/973 646 Group: 1714

Confirmation No.: 6210

Filed: October 9, 2001 Examiner: Shosho

Atty. Docket No.: Nanjo Case 1

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

**EXCUSE FOR FAILURE TO OBTAIN
JOINT INVENTOR'S SIGNATURE**

As evidenced by the attached death certificate and English-language translation thereof, Kazuo HARUTA died on April 16, 2004 and, therefore, was unable to sign the Declaration Under 37 CFR 1.131.

Date 5-24-04 Terryence F. Chapman
Terryence F. Chapman
Reg. No. 32 549

Attachment: Death Certificate and
English Translation thereof



VERIFICATION OF TRANSLATION

I, Tomoko Yamaguchi of 4-12-16-407, Nagata, Jyoto-ku, Osaka 536-0022, Japan

declare as follows:

That I am well acquainted with both the English and Japanese languages, and

That the attached document is a partial and faithful translation made by me to the best of my knowledge and belief of:

Certificate for All Hysteresis Matters

Date: May 21, 2004

Tomoko Yamaguchi

(Signature of Translator)

(Partial Translation)

CERTIFICATE FOR ALL HYSTERESIS MATTERS

Permanent Address: **429 Nishiki-machi, Yamaguchi-shi,
Yamaguchi**

Name: **Kazuo HARUTA**

Status:

Death

Date of Death: **April 16, 2004**

Time of Death: **11:52am**

Place of Death: **Yamaguchi-shi, Yamaguchi**

Date of a Notice of Death: **April 16, 2004**

Person of Notice: **a relative, Setsue HARUTA**

Issue No. 00140831

**It is a document to be certified that these are all matters to
be recorded in the register.**

May 6, 2004

A Mayor of Yamaguchi-city, Eiichi GOHSHI

(Seal)

| | |
|-----------------------|--|
| 本籍 氏名 | 山口県山口市錦町429番地 春田 和夫 |
| 戸籍事項 戸籍改製 | 【改製日】平成12年3月25日 【改製事由】平成6年法務省令第51号附則第2条第1項による改製 |
| 戸籍に記録されている者 除籍 | 【名】和夫 【生年月日】昭和26年12月12日 【父】春田正己 【母】春田武子 【続柄】四男 |
| 身分事項 出生 | 【出生日】昭和26年12月12日 【出生地】山口県山口市 【届出日】昭和26年12月24日 【届出入】父 |
| 婚姻 | 【婚姻日】平成10年10月28日 【配偶者氏名】松井勢津恵 【従前戸籍】山口県山口市錦町429番地 春田正己 |
| 死亡 | 【死亡日】平成16年4月16日 【死亡時分】午前11時52分 【死亡地】山口県山口市 【届出日】平成16年4月16日 【届出入】親族 春田勢津恵 |
| 戸籍に記録されている者 | 【名】勢津恵 【生年月日】昭和31年2月17日 【父】藤井一 【母】藤井和子 【続柄】二女 |
| 身分事項 出生 | 【出生日】昭和31年2月17日 【出生地】山口県宇部市 【届出日】昭和31年2月23日 【届出入】父 |
| 婚姻 | 【婚姻日】平成10年10月28日 【配偶者氏名】春田和夫 【従前戸籍】山口県山口市楠木町4番 松井勢津恵 |

発行番号 00140831

以下次頁

(2の2) 全部事項證明

以下余白

| | |
|--------|---------------------|
| 配偶者の死亡 | 【配偶者の死亡日】平成16年4月16日 |
| | |

発行番号 00140831

これは、戸籍に記録されている事項の全部を証明した書面である。

平成16年5月6日

山口市長

合志 栄

